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TRANSPORT DE MOTT

METAL-INSULATOR TRANSITIONS
IN TRANSITION METAL OXIDES

by D. B. McWHAN, A. MENTH and J. P. REMEIKA

Bell Telephone Laboratories, Incorporated Murray Hill, New Jersey

Résumé. — Dans les oxydes de métaux de transition on observe une transition d'isolant à métal puis de métal à isolant de type Mott lorsque l'on augmente le nombre d'électrons d. Dans le système $(V_{1-x}Cr_x)O_3$, une transition de Mott apparaît pour $x = 0.01$. À haute température $V_2O_3$ et $(V_{0.99}Cr_{0.01})O_3$ ont des résistivités et des coefficients de température de la résistivité analogues. Des mesures de susceptibilité magnétique et de résistivité sur $V_xO_{3+x}$ montrent que l'état isolant antiferromagnétique est supprimé par un excès d'oxygène pour $x \approx 0.03-0.04$. On remarque que des impuretés trivalentes stabilisent l'état isolant alors que des ions non trivalentes favorisent l'état métallique.

Abstract. — There is a transition from band insulator to metal to Mott insulator with increasing number of d electrons in the transition metal oxides. In the $(V_{1-x}Cr_x)O_3$ system a Mott transition occurs near $x = 0.01$. At high temperatures $V_2O_3$ and $(V_{0.99}Cr_{0.01})O_3$ are found to have similar resistivities and temperature coefficients of resistivity. Magnetic susceptibility and electrical resistivity measurements on $V_xO_{3+x}$ show that the antiferromagnetic insulating state is suppressed by excess oxygen at $x \approx 0.03-0.04$. It is pointed out that trivalent impurities stabilize the insulating state whereas predominantly non-trivalent ions favor the metallic state.

I. Introduction. — Transition metal oxides form a class of materials in which one can study experimentally both metal-insulator transitions and the onset of long range magnetic order. In 1946 Foex found that $V_2O_3$ has a temperature induced metal-insulator transition [1]. Since then it has become evident that a large number of other oxides of vanadium and titanium also have metal insulator transitions. In good single crystal samples the accompanying changes in the resistivity are several orders of magnitude (e. g. VO$_2$, [2, 3, 4] V$_4$O$_7$, [5] V$_5$O$_{12}$, [6] Ti$_2$O$_7$, [7], etc.). Most of the transition metal oxides with more than 2 d electrons per transition metal atom, are magnetic and insulating both above and below their ordering temperatures. These oxides are believed to be insulating because the ground state wave function is a localized or Heitler-London type as a result of the strong Coulomb repulsion between the d electrons. The nature of the transition from a Bloch-Wilson or band description to a localized or Heitler-London description has long been of theoretical interest. In 1949 Mott suggested that such a transition would be discontinuous as a function of volume [8], and he later proposed a phase diagram for a first order transition between a degenerate electron gas and a localized antiferromagnetic insulator at low temperatures [9]. Serious questions have arisen about the nature of this transition (see Proceedings of the Conference on the Metal-Nonmetal Transition held in San Francisco in 1968) [10], and it is fair to say that a detailed microscopic theory does not exist at the present time. However, there are a number of compounds from which it is possible to gain experimental insight into the problem. In the following paper the transition metal oxides are discussed within the framework of the periodic table, and recent results are presented on the mixed oxide systems $(V_{1-x}Cr_x)O_3$, $(V_{0.99}Al_{0.01})O_3$ and $V_xO_{3+x}$ where $0 \leq x \leq 0.12$. The metal insulator transition in these systems is found to have all the qualitative features expected for a Mott transition [11]. More detailed experimental results on the $(V_{1-x}Cr_x)O_3$ system are given in Ref. [12-21] and theoretical discussions of the metal insulator transition can be found in ref. [10, 23, 24]. Finally, a discussion of the qualitative differences between $V_2O_3$ and the class of materials consisting of VO$_2$ and the Magnéli phases $(Ti_xO_{2n-1})$ and $V_xO_{3n-1}$ where $n \geq 4$ was given in an earlier paper [25].

II. Trends in transition metal oxides. — In figure 1 the properties of a number of oxides are summarized by arranging them according to oxidation state (x in

![Fig. 1. — Periodic arrangement of transition metal oxides $MO_x$ with $x$ plotted versus $M$. The shading shows the regions of stability of band insulators, Mott insulators and magnetism. Note large number of materials in between which show temperature induced insulator to metal transitions.](http://dx.doi.org/10.1051/jphyscol:19711388)
MO₃) on the ordinate and transition metal M on the abscissa. An approximate separation of the conducting properties into three regions can be made as shown by the shading. In the upper left the oxides have no d electrons, and they are insulators which can be described in terms of normal Bloch-Wilson band theory. On the right the materials are Mott insulators and are best described using a Heitler-London or localized approach. In the intermediate region the materials are usually metallic near room temperature and many have a transition to an insulating state with decreasing temperature. Some, such as TiOₓ (0.8 < x < 1.2) and CrO₃, are metallic at all temperatures. While others have continuous transitions from semiconducting to metallic behavior as a function of temperature (TiO₂) or as a function of composition (VOₓ with x decreasing from 1.2 to 0.8).

Magnetic ordering is only found in the materials on the right side of figure 1 and it seems to occur in the higher oxides when there are two or more d electrons per metal atom. Although a Mott insulator is magnetic, the magnetic properties of the metallic state are more subtle as V₂O₅ is a paramagnetic metal at high pressure but CrO₃ is a ferromagnetic metal. Sometimes when there are two different transition metals, as in the case of CrVO₄, the lattice distorts to give V⁵⁺ and Cr³⁺ ions, and the material is an antiferromagnetic insulator.

It is evident that V₂O₃ is at the critical region both for the metal-insulator transition and for the onset of magnetism. In the next section these transitions are explored by 1) doping with other metal ions 2) varying the oxygen stoichiometry and 3) using the pressure variable.

III. Transitions in mixed oxides of V₂O₃. — V₂O₃ has a first order transition with decreasing temperature at ≈ 150 °K from the metallic, trigonal, corundum structure to an antiferromagnetic, insulating, monoclinic structure. The resistivity change at the transition is > 10⁷ in good single crystals. Near 500 °K there is an anomaly which is marked by continuous changes in the lattice parameters, resistivity, magnetic susceptibility and many other properties. Examination of figure 1 suggests that V₂O₃ should be considered as part of a more general phase diagram.

Recently, this diagram has been established for the (V₁₋ₓCrₓ)O₃ system with the aid of the pressure variable (Fig. 2 inset) [11]. The addition of 1 % Cr₂O₃ to V₂O₃ results in a first order transition with no change in crystal structure from a metallic (M) to an insulating (I) state at room temperature. (Note changes in magnitude and in the temperature dependence of the resistivity in figure 2.) A transition back to the metallic phase occurs with increasing pressure. With decreasing temperature both the metallic (M) and insulating (I) phases transform to the antiferromagnetic insulating (AF) phase. The M-AF transition temperature is a strong function of pressure, and in V₂O₃ the AF phase is suppressed completely by pressures in excess of 26 kbars [26].

By constructing a pressure-temperature-composition diagram one can show that the high temperature anomaly in V₂O₃ represents an extension of the M-I transition surface [12]. It has been shown experimentally that the M-I boundary terminates at a solid-solid critical point [13] and that the transition in V₂O₃ is a continuous transition above the critical point. There are discrepancies in the literature about the resistivity anomaly at high temperature in V₂O₃. The data of Foex [27] show that the resistivity of ceramic samples decreases with increasing temperature above the anomaly; whereas the data of Feinleib and Paul [28] and of Austin and Turner [29] taken on single crystals show an increase with increasing temperature. We have extended our resistivity measurements to higher temperatures and the results are shown in figure 2. Single crystals of V₂O₃ and (V₀.₉₉Cr₀.₀₁)O₃ from the earlier studies were used [11]. Four probe ac measurements (using pressure contacts) were made on the samples which were heated in 1 atm. of argon. It was found that the resistivity measurements were only reversible up to temperatures of 800 °K. A negative temperature coefficient is observed between 550 °K and 800 °K for V₂O₃ in agreement with the data of Foex and compatible with insulating behavior as is observed for the Cr doped samples. The resistivity of V₂O₃ and the 1 % Cr doped sample approach one another and have similar slopes.
at high temperature (see Fig. 2). After holding the sample at temperatures above 800 °K one finds that the resistivity of \( V_2O_3 \) becomes time dependent and approaches the behavior observed in Ref. [28 and 29].

One infers from these experiments that deviations in the stoichiometry can account for the different results reported in the literature.

Besides Cr, it has been found that the addition of Al or Fe will result in an M-I transition at room temperature. For approximately 1 % \( Al_2O_3 \) or \( Cr_2O_3 \) in \( V_2O_4 \) the sequence \( I \rightarrow M \rightarrow AF \) is observed with decreasing temperature. This sequence is seen in the magnetic susceptibility and NMR results of Menth, Gossard and Remeika on the \((V_1-x Al_x)_2O_3 \) system [19]. X-ray results for a powdered sample of \( V_{0.99}Al_{0.01}O_3 \) are shown in figure 3. The experiments were done in the same way as the earlier work in the V-Cr system [12]. With decreasing temperature there is a first order transition in which \( c_h \) contracts and \( c_H \) expands, but there is no observable change in crystal structure. At lower temperatures a transition to the monoclinic AF phase occurs, and the observed lattice parameters are similar to those found in the V-Cr system [11].

![Figure 3](image)

**Fig. 3.** — The lattice parameters versus temperature for 1 % \( Al_2O_3 \) in \( V_2O_3 \) showing first order transition with no change in crystal structure at \( \approx 250-350 \) °K. At low temperatures there is a transition to the monoclinic antiferromagnetic phase.

Returning to figure 1, the results on the \((V-Cr)_2O_3 \) mixed oxide system establish that a sharp metal-insulator transition exists as a function of composition and of pressure (Fig. 2 inset). The transition at low temperatures is from a paramagnetic metal at high pressure to an antiferromagnetic insulator. On the other hand the higher oxides of vanadium are insulating but not magnetically ordered at low temperatures and 1 atm. The work of Nakahira, Horiuchi and Ooshima [30] suggests that a transition from an antiferromagnetic to a paramagnetic phase occurs with increasing \( x \) in \( V_2O_{3+x} \) before the transition to the region of stability of the \( V_3O_5 \) phase is reached. These authors showed that there are no deviations from Curie-Weiss behavior down to 77 °K in the magnetic susceptibility of \( V_2O_{3.068} \) and also no crystallographic distortion to the monoclinic structure. In the present work electrical resistivity and magnetic susceptibility measurements have been made down to liquid helium temperatures on pressed powder samples containing excess oxygen. Also, resistivity measurements have been made at high pressure in order to establish a pressure-temperature-composition phase diagram for \( V_2O_{3+x} \).

The samples of \( V_2O_{3+x} \) were prepared by ball milling in ethyl alcohol appropriate amounts of \( V_2O_3 \) and \( V_2O_5 \). After ball milling, the slurry is immediately vacuum filtered and air dried. The sample was pressed into a pellet and heated in an evacuated quartz tube 1000 °C for approximately 50 hours. It is difficult to obtain reliable analysis of the oxygen content of transition metal oxides, and it was assumed that no oxygen was gained or lost during the heat treatment. Although this assumption is somewhat questionable, a smooth change in oxygen stoichiometry from sample to sample should result as they were all prepared in the same way. The samples were checked by powder X-ray diffraction methods, and a small amount of a second phase, \( V_3O_5 \), is seen in Guinier powder patterns as the amount of excess oxygen increases above \( V_2O_{3.04} \). The lattice parame-
ters resulting from a least squares refinement of the high angle powder diffraction data obtained using a Debye Scherrer camera and filtered CrKα radiation are shown in figure 4. Also included are data from the work of Nakahira, et al. [30]. Both sets of experiments show a smooth change in lattice parameters up to \( x \approx 0.04-0.06 \) in \( V_2O_3+x \) and then the parameters become less dependent on \( x \). As this change in slope coincides with the appearance of \( V_3O_5 \), it suggests that the limit of excess oxygen in the corundum phase is \( x \approx 0.04-0.06 \). The reason for the discrepancies between the present work and that of Nakahira, et al. is unclear. The samples were made at different temperatures and the stoichiometry determined in different ways so a direct comparison may not be meaningful. The experiments by Foex [21] and of MacMillan [31] show that the properties of \( V_2O_3 \) depend on the temperature at which the samples were prepared. Electrical resistivity measurements were made at 1 atm. by spring loading four probes onto bars cut from the pressed powder samples. Resistivity measurements on pressed powders are of a qualitative nature and therefore no significance can be attached to details of the observed resistivity in the M and AF phases. The results of a series of warming curves on representative samples are shown in figure 5. The metal (M) to antiferromagnetic insulator (AF) transition temperature decreases rapidly with increasing \( x \), and the insulating state is suppressed between \( x = 0.030 \) and 0.035. This strong dependence of the transition temperature on stoichiometry probably accounts for the wide range of transition temperatures reported in the literature for \( \langle V_2O_3 \rangle \).

![Fig. 5. — Resistivity versus increasing temperature for pressed powder samples of \( V_2O_3+x \). M-AF transition is suppressed between \( x = 0.030 \) and 0.035.](image)

The antiferromagnetic insulating phase of \( V_2O_3 \) is suppressed by pressures in excess of 26 kbars. The variation of the critical pressure with stoichiometry was determined from four probe resistivity measurements as a function of temperature and pressure using experimental techniques that have been described elsewhere [12]. In each experiment the pressure was increased at room temperature to a pressure in excess of the estimated critical pressure \( P_c \). The sample was cooled to 4.2 K and the pressure cycled through the M-AF transition. In the earlier experiments on single crystal samples of \( V_2O_3 \) the M-AF transition at 4.2 K was characterized by an abrupt increase of \( > 10^2 \) in the resistivity over a pressure range of less than a kbar. In the pressed powders in the girdle die there are probably large pressure and composition gradients, and the M-AF transition was spread over a pressure range of \( \sim 5 \) kbars.

From the measurements at 1 atm. and at high pressure on \( V_2O_3 \) and \( V_2O_3+x \) a three dimensional pressure-temperature-composition phase diagram was constructed and it is shown in figure 6. Because of the broadness of the transition in pressed powder samples and because of the uncertainty in the absolute stoichiometry of the different samples the phase diagram is only a semiquantitative measure of the effect of excess oxygen on the M-AF transition. There is hysteresis in the transition as indicated by the different points, and a single average surface was drawn. Nonetheless, figure 6 shows that the M-AF transition is a strong function of both pressure and stoichiometry.

![Fig. 6. — Temperature-pressure-composition phase diagram for \( V_2O_3+x \) showing the suppression of the antiferromagnetic insulating phase. Curve for \( V_2O_3 \) is from Ref. [26]. Circles and triangles are for increasing and decreasing pressure or temperature.](image)

Returning to figure 5, the curves for samples with \( x = 0.035 \) and 0.040 show a rise in the resistivity with decreasing temperature below 100 K. This is in contrast to the data obtained on single crystals of \( V_2O_3 \) above the critical pressure which showed a strong \( T^2 \) dependence of the resistivity at low temperatures [25]. It is not clear if this rise is an intrinsic property of the oxygen rich phase or if there are small regions of the sample which still have an M-AF transition as a result of inhomogeneities or local strains in the pressed power samples. In an attempt
to resolve this question measurements of the resistivity as a function of temperature were made on pressed powders of V$_2$O$_3$ and V$_2$O$_{3.02}$ at different pressures. The results are summarized in figure 7 and compared to earlier results obtained using single crystal samples of V$_2$O$_3$. The results in both experiments were reversible in that the $\rho$ vs. $T$ curves taken after releasing pressure were in fair agreement with the curves obtained on increasing pressure. At 26 kbars the pressed powder sample does not agree with the single crystal measurements but with increasing pressure the curve is becoming similar to the crystalline results. The V$_2$O$_{3.02}$ sample also approaches the behavior of crystalline V$_2$O$_3$ at fairly high pressures. These results suggest that the rise in resistivity in V$_2$O$_{3.04}$ may reflect inhomogenieties, but the measurements should be repeated on single crystal material.

![Graph](image1)

**Fig. 7.** Comparison of resistivity versus temperature for pressed powder samples of V$_2$O$_{3-x}$ and single crystal samples of V$_2$O$_3$ at different pressures above the critical pressure shown in figure 6. V$_2$O$_3$ single crystal data from Ref. [26].

The magnetic susceptibility $\chi$ of samples with $x = 0.00, 0.02, 0.03$ and 0.04 were measured, and the results are shown in figure 8. The increase in $\chi$ at low temperatures which is observed in the powder sample of V$_2$O$_3$ is in contrast to the single crystal material which shows no increase in $\chi_1$ and $\chi_2$ relative to the c-axis. This may be due to the alignment of the antiferromagnetic axes [14] by particle reorientation in an external magnetic field. The samples with excess oxygen show an additional increase of $\chi$ since at low enough temperatures $\chi$ exceeds its value at the transition temperature. The sample with $x = 0.04$, which does not have a M-AF transition in the resistivity (Fig. 5), also has the additional increase in susceptibility. A plot of $1/\chi$ versus $T$ shows a change in slope at the same temperature at which the resistivity starts to increase. When well characterized crystals of V$_2$O$_{3+x}$ are made it will be interesting to study these anomalies in the resistivity and $\chi$ as they may reflect the incipient M-AF transition as a function of oxygen stoichiometry.

The effect of adding oxygen is to make V$_2$O$_3$ more metallic similar to the role of pressure. On the other hand adding Cr$_2$O$_3$ makes the system less metallic. It is of interest to see to what extent these variables act independently. A ceramic sample of (V$_{0.93}$Cr$_{0.04}$)$_2$O$_3$ was made and the resistivity measured versus temperature. The sample was then powdered and mixed with 2% V$_2$O$_3$ and pelletized and fired. The resistivity versus temperature for the two samples is shown in figure 9. The Cr made the sample insulating at all temperatures and the addition of oxygen produced a drop in the resistivity at intermediate temperatures similar to, but much broader than, the sequence of
transitions found in \((V_{0.99}Cr_{0.01})_2O_3\) i.e. \(I \rightarrow M \rightarrow AF\) with decreasing temperature (see Fig. 2). In an experiment at high pressure, a rather broad M-AF transition was observed at 4.2 °K with a critical pressure of \(\approx 11\) kbars and \(\approx 7\) kbars for increasing and decreasing pressure respectively.

IV. Discussion. — In the transition metal oxides, experimentally the compounds pass from a metallic region to a magnetic insulating region with increasing number of d electrons. The results on the \((V_{1\rightarrow-Cr_2})_3O_3\) system show that this transition from band to localized behavior at lower temperature is discontinuous.

Below the critical point the transition is first order but with no observable change in long range order. Studies of different physical properties such as magnetic susceptibility [14], nuclear resonance, [15, 19] Mößbauer resonance, [18] optical properties [21] and electrical resistivity support the picture of a transition from a band metal to a localized insulator. This system has, therefore, all the qualitative features originally suggested by Mott [8, 9]. The transition was visualized as a function of volume and in fact pressure studies on the \((V_{1\rightarrow-Cr_2})_3O_3\) system do establish an I \(\rightarrow\) M transition with increasing pressure. However, it is not clear why the addition of chromium should result in a Mott transition. Experimentally it is known that the addition of Ti or Mg stabilizes the metallic phase [31] as does excess oxygen. On the other hand the addition of Al, Cr, Sc [12, 31] or Fe [18, 32] stabilizes the insulating phase. One cannot argue in terms of changing the Fermi level within a rigid band model because Al and Sc have no d electrons. However, a rigid band model is not expected to be applicable in a highly correlated system such as \(V_2O_3\). A size effect argument cannot be invoked because \(\Delta^{3+}\) is smaller than \(V^{3+}\) but \(Sc^{3+}\) is larger. A consistent picture does seem to emerge from considering the stability of the oxidation state of the metal ions. All the ions which stabilize the insulating state are trivalent. Whereas most of those which stabilize the metallic state are not trivalent: Mg\(^{2+}\) and V\(^{4+}\) (excess oxygen, see below). In Ti both the +4 state and the +3 state are stable, and in Fe both the +2 state and the +3 state are stable. As two states are possible the effect of adding Ti and Fe is much less clear than that of adding the other ions. A much larger concentration of Fe is needed to stabilize the insulating state than is needed for the other predominantly +3 ions. In the insulating state the number of electrons on a metal ion is essentially constant; while in the metallic state the number of course fluctuates. Therefore, the impurities which prefer the trivalent state will inhibit fluctuations and tend to stabilize the insulating phase. Perhaps we can view this process crudely as an increase in the average strength of the intra-atomic Coulomb interaction which drives the system through the metal-insulator transition. On the other hand, the +2 and +4 impurities will increase the carrier concentration and favor the metallic state.

The nature of the oxygen rich \(V_2O_3\) samples should be considered in the light of the overall crystal chemistry of the Ti and V oxides. The body of structural information on the higher oxides suggests that there will not be random vanadium vacancies in the hexagonally close packed oxygen structure [33]. Instead there will probably be Wadsley defects similar to those found in reduced rutile [33, 34]. In the latter case the environment at the defect resembles a block of the corundum structure. The corundum structure itself can be described as being built up of blocks of rutile which are infinite in two dimensions and two octahedra wide in the third dimension [32]. In \(V_2O_3+x\) some of the blocks would be more than two octahedra wide. This would have the effect of putting sheets of \(V^{4+}\) ions similar to \(VO_2\) through the crystal.

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